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MULTIFUNCTIONAL CHARGES FOR OBTAINING PROTECTIVE COATINGS ON PRESSING EQUIPMENT UNDER SHS CONDITIONS

Multifunctional SHS charges for the production of chrome coatings alloyed with titanium and silicon have been developed in this work in order to strengthen the working surfaces of press tooling dies used in aggressive conditions during the vulcanization of products made of elastomeric materials. Pressing is performed on a hydraulic vulcanizing press 100-400 2E. with plate sizes 400x400 of new elastomeric materials based on 10 wt.% carbonized PAN fiber (RC Helper), which significantly increases the heat capacity of rubber based on a copolymer of vinyl di-fluoride and hexopropylene by 15-30% in the operating temperature range from 323 to 348 K. One of the newest and most effective technologies for manufacturing a wide range of materials, including composite materials, is the SHS technology, which is based on the direct synthesis of compounds of practical value in exothermic reactions between certain chemical elements. Protective coatings on samples under SHS conditions were obtained at the developed pilot plant DSTU12, which consists of the following main functional systems: reaction equipment; system for monitoring and controlling technological parameters; gas utilization system. Samples from 45 and 40X steels were used for coating. Mixtures of powders with a dispersion of 100-250 microns of the following materials were used as reaction agents. Using a three-factor, three-level composite asymmetric plan of the second order, the optimal blends for obtaining protective alloy coatings were developed. The resulting coatings are characterized by a multiphase structure and thickness uniformity. For titanium-doped chromium coatings obtained on samples from steel 45, the phases $(Cr,Fe)_{23}C_6$, $(Cr,Fe)_7C_3$, Fe_2Ti, Cr_2Ti, and α-solid solution of titanium and chromium in α-iron were found. For 40X steel, the phases $(Cr,Fe)_{23}C_6$ and α-solid solution of chromium in iron with Cr_2Ti inclusions alloyed with titanium are formed.

Key words**:** charge, chrome, coatings, press tooling, self-propagating high-temperature synthesis, rubber products.

Introduction. Today, composite materials, such as rubbers and tires based on natural or synthetic rubber, are widely used in metallurgy, textiles, and chemicals. The use of rubber materials makes it possible to manufacture structural elements and tribotechnical products with high damping characteristics, excellent elasticity and corrosion resistance. In addition, the replacement of metals with rubber can reduce the material consumption of equipment and shorten production time, even for complex parts, while increasing their resistance to corrosion [1]. Modern operating conditions for machine parts, assemblies, equipment, tools and mechanisms place increased demands on their physical and mechanical characteristics and service life. The role of surface hardening processes in the durability of machines and mechanisms has especially increased at present, as the development of machine-building industries is associated with increased loads and temperatures at which critical parts operate under aggressive conditions on equipment for vulcanizing products made of new elastomeric materials. The development of many areas of modern industry is impossible without the development and use of new resource-efficient technologies. In this case, an important role is played by technologies that can impart special properties to surface layers. To the greatest extent, these requirements are met by the SHS technology, which makes it possible to produce materials and coatings with adjustable composition, structure and performance characteristics.

Analysis of recent research and publications. For pressing new elastomeric materials, we used simultaneous mechanical loading and temperature exposure, which is necessary for vulcanization of rubber compounds in molds. The maximum force during pressing reached

1000 kN. As for the method of self-propagating high-temperature synthesis (SHS), its essence is to initiate a reaction between powder components, which is accompanied by heat generation and spontaneous propagation of the reaction wave. According to the type of chemical reactions, SHS processes are divided into three main groups: direct synthesis from elements, synthesis from compounds and exchange reactions, and metallothermal reactions [2]. The products of such processes include carbides, borides, silicides, nitrides, intermetallics, and other compounds. Depending on the state of the reagents and products, SHS processes are divided into gas-free, low-gas, filtration, and metallothermal [3]. Modern operating conditions for machine parts, assemblies, equipment, tools and mechanisms place increased demands on their physical and mechanical characteristics and service life. The role of surface hardening processes in the durability of machines and mechanisms has especially increased at present, as the development of machine-building industries is associated with increased loads and temperatures at which critical parts operate under aggressive conditions on equipment for vulcanizing products made of new elastomeric materials [4]. The development of many areas of modern industry is impossible without the development and use of new resource-efficient technologies. In this case, an important role is played by technologies that can impart special properties to surface layers. To the greatest extent, these requirements are met by the SPS technology, which allows to produce materials and coatings with controlled composition, structure and performance characteristics. The essence of the SHS method is to carry out exothermic reactions in the mode of combustion wave propagation with the formation of combustion products in the form of material compounds that have practical value and valuable characteristics [5–6]. The regularities of combustion wave propagation in SHS processes are numerous and can be controlled by various parameters, for example, by changing the ratio of reagents, varying the degree of dilution of the charge with inert products, heating the charge, etc. The influence of these parameters, the ultrafast front propagation, is mainly due to changes in the combustion temperature. A method of lowering the combustion temperature in SHS processes is dilution of the starting substances with combustion products, and a method of increasing it is preheating the charge. The SHS processes and products are widely used in various industries: mechanical engineering (abrasives, tool and construction materials, ceramics), metallurgy (ferroalloys and ligatures), chemical industry (refractory compounds, fumigants, pigments, catalysts), inorganic materials technology (for producing powders, compact materials and products, coating and welding parts), creation of functional gradient materials, production of single crystals, phosphors, high-temperature superconductors and nanomaterials [7–8].

Statement of the problem. The purpose of our research is to obtain multicomponent chrome coatings alloyed with titanium and aluminum in order to strengthen the working surfaces of parts operated under aggressive conditions on equipment for vulcanizing products from new elastomeric materials using modern methods of surface hardening of materials, including the SHS technology, with the main goal of developing new approaches to improve the mechanical properties and extend the service life of materials. As part of this study, a broad review of existing methods for obtaining protective coatings was conducted, and the features of the SHS processes were thoroughly studied. Experimental studies were carried out to determine the optimal process parameters, as well as to analyze the data obtained in order to determine the effectiveness of the SHS method for improving the mechanical properties of materials and extending the service life of machine parts and press equipment.

Presentation of the main material. Coatings produced under SHS conditions have unique properties. They are formed from a layer of deposited product, similar to the process of vapor deposition, and include a wide transitional diffusion zone, which resembles diffusion saturation. Due to this, SHS coatings demonstrate improved characteristics compared to other analogues: for example, increased wear or heat resistance compared to the base material, as well as high adhesive strength between layers of powders, where particles of one material are covered with a layer of another [9]. This creates a significant contact area between the reagents, especially when using finely dispersed particles.

Prerequisite for obtaining new materials with an optimal set of effective properties is the development of technologies of a qualitatively new level, based on the understanding and prediction of structure formation processes, and, consequently, the ability to influence the mechanism of structure formation with the desired physical and mechanical properties. One of the newest and most effective technologies for manufacturing a wide range of materials, including composite materials, is the SHS technology, which is based on the direct synthesis of compounds that are valuable in practical terms in exothermic reactions between certain chemical elements. The SHS method allows to produce refractory compounds of various chemical and phase compositions (carbides, nitrides, silicides, chalcogenides, intermetallics, hydrides), as well as reduced metals. In addition, the SHS method can produce inorganic materials with different physical properties (powdered; sintered - solid and porous; cast), as well as products of certain shapes and sizes.

In the work, samples from mass-produced steels Steel 45 and 40X were used for coating. Mixtures of powders with a dispersion of 100-250 microns of the following materials were used as reaction agents. In determining the required dispersion of the reagents, we were guided by studies that found that the maximum completeness of the transformation is observed when using a reaction mixture with a fraction of 100-120 microns. The protective coatings on the samples under the conditions of the SIS were obtained using the developed pilot plant DSTU12, which consists of the following main functional systems: reaction equipment; system for monitoring and controlling technological parameters; gas utilization system.

To apply protective coatings to steel samples, such as steel 45 and 40X, mixtures of powders with different dispersions ranging from 100 to 250 microns were used. These powders included elements such as chromium, silicon, boron, aluminum oxide, aluminum, iodine, and ammonium fluoride. The choice of powder dispersion was based on studies that showed that the optimal powder fraction for achieving maximum reaction completeness is from 100 to 120 microns. The working surface after treatment with SHS on a hydraulic vulcanization press 100-400 2E, under the conditions of the current production, is shown in Fig. 1.

Currently, composite materials (rubbers, rubber) based on natural and artificial rubber have become an integral part of the metallurgical, textile and chemical industries. The use of rubbers makes it possible to produce structural and tribotechnical products characterized by enhanced damping properties, high elasticity and corrosion resistance. In addition, the use of rubbers instead of metals reduces the material consumption of structures and machines, shortens the production time of parts (even those with complex configurations), and increases corrosion resistance. Pressing was carried out on a hydraulic vulcanizing pressing machine 100-400 2E with plate sizes of 400x400 new elastomeric materials based on a copolymer of vinyl dlfluoride and hexopropylene, ethylene-propylene rubber, containing carbonized polyacrylonitrile fiber, stone (granite) flour, and aluminosilicate microspheres. Rubber is a mixture of substances, the main component of which is natural or artificial rubber. It is known that pure rubber is characterized by low mechanical, thermal, chemical and electrical properties [10]. Effective fillers for natural and artificial rubbers are clay, carbon black, modified montmorillonite octadecylamine, silica (SiO_2), aluminosilicate hollow microspheres (AHM), technical carbon.

Fig. 1 – Work surface after processing of the SHS on a hydraulic vulcanizing press

Rubber-based composites may prove to be competitive and eventually replace traditional materials in a number of applications, as there are many advantages to using these materials. For example, rubber-based composites often have a lower density than traditional materials such as metals. This leads to a reduction in the weight of products, which is important in a variety of industries where lightness is a key characteristic. Rubber composites are characterized by shock absorption, flexibility, and elasticity, which makes them capable of handling dynamic loads and adapting to various forms of deformation without losing structural properties. Compared to metals, rubber composites can be less susceptible to corrosion, making them more durable and less costly to maintain in some operating conditions. The ability of rubber to insulate thermally makes them attractive for applications in construction and other industries where thermal insulation is important [11–12].

However, it is important to take into account limitations and challenges, such as limited strength compared to metals, possible problems with heat dissipation at high temperatures, and the cost of producing and processing rubber composites. The growth in demand for these materials will depend on technological development, solving these problems and increasing their competitiveness in the market.

Existence of limiting temperatures at which the combustion front can propagate places certain restrictions on the use of the combustion mode in technologies. On the contrary, the thermal autoignition mode is free from these limitations. By diluting the initial powder mixture with an inert substance to 85-90% of the mass, it is possible to reduce the maximum temperature of the process to a technologically necessary level. As the temperature increases, the number of products in the gaseous phase increases and condensed products are released.

Using a three-factor, three-level compositional asymmetric plan of the second order, the optimal blends for obtaining protective coatings alloyed with titanium were developed. The choice of the main level and intervals of variation is based on the fact that the introduction of a chromium component less than 10% by weight leads to a disruption of the combustion wave of thermal spontaneous combustion. The amount of chromium component is selected based on the study of changes in the characteristic temperatures of the SHS process. To obtain one hundred percent composition of powdered SHS charges, Al_2O_3 is used as a ballast impurity:

$$Y_1 = 32{,}889 + 2{,}1X_1 + 0{,}8X_2 + 0{,}7X_3 + 1{,}3889X_1^2 - 0{,}1111X_2^2 - 1{,}6111X_3^2 + 0{,}25X_1X_2 - 1{,}25X_1X_3 - 0{,}25X_2X_3$$

$$Y_2 = 173{,}64 - 0{,}8X_1 - 3{,}3X_2 - 2{,}4X_3 + 0{,}4444X_1^2 + 6{,}9444X_2^2 + 0{,}4444X_3^2 + 0{,}25X_1X_3 - 1{,}25X_2X_3$$

Mathematical planning of the experiment significantly reduces the number of studies required to calculate the coefficients of the regression equation and obtain an adequate model that characterizes the effect of the elements of the SHS charge on the performance properties of steels with alloy protective coatings. The response surfaces of the obtained mathematical models are represented by three-dimensional graphical dependencies (fig. 2).

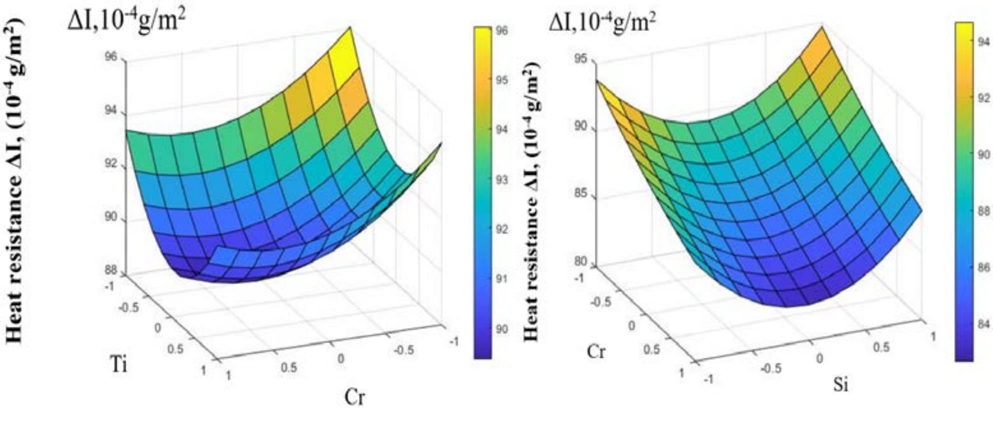
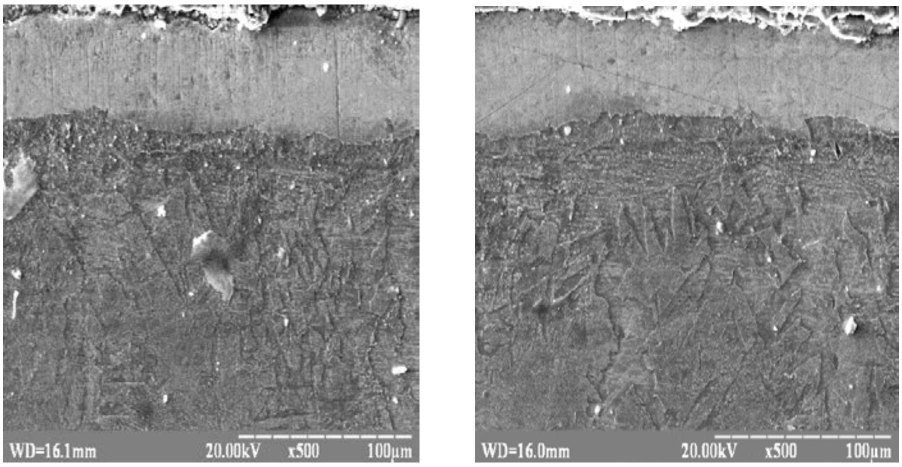


Fig. 2 – Graphical dependencies of mathematical planning of the experiment

Based on the results of the mathematical planning of the experiment, multifunctional blends were developed to produce heat-resistant chrome coatings: when alloyed with titanium 25% XC + 15% Cr + 20% Ti+ 34% Al_2O_3 + 2% J_2+ 4% NH_4Cl, when alloyed with silicon 24% XC + 15% Cr + 7% Si+ 49% Al_2O_3 + 2% J_2+ 3% NH_4Cl.

For solving problems requiring operational control when obtaining protective coatings in the conditions of the SHS, only scanning electron microscopy is most suitable. In this work, we used a SEM-106i, a scanning electron microscope with a low vacuum chamber. The preparation and processing of the cross-sectional grinds was carried out according to the standard method. To reveal the microstructure of coatings obtained on steels, a 3% alcohol solution of picric acid in ethyl alcohol was used (fig. 3).



a b

Fig. 3 – Microstructures of titanium alloyed chrome coatings (t_p – 1000 °C, τ_t=30 хв.): a – steel 45; b – steel 40X

The resulting coatings demonstrate a complex multiphase structure and are also characterized by a high degree of uniformity in thickness. The chromium contained in the coatings shows a more uniform distribution of concentration peaks both in the surface zone and in the transition region. This indicates the active participation of chromium in the formation of phases such as $(Cr,Fe)_{23}C_6$ та $(Cr,Fe)_7C_3$, and also promotes the formation of a solid solution of aluminum and chromium in α-iron.

The following phases were found in the titanium-alloyed chrome coatings obtained on samples of steel 45 $(Cr,Fe)_{23}C_6$, $(Cr,Fe)_7C_3$, Fe_2Ti, Cr_2Ti and α- solid solution of chromium and titanium in the matrix α-Fe. These phases provide high hardness and strength of the coatings, which contributes to their durability and increased wear resistance. In the case of 40X steel, similar phases are observed: $(Cr,Fe)_{23}C_6$ and α-solid solution of chromium in iron, doped with titanium, with inclusions Cr_2Ti.

The phase composition of such coatings is explained by the fact that under SHS conditions, chromium reaches a liquid state and can actively diffuse into the substrate, forming a uniform structure. Titanium, in turn, has a lower diffusion activity, which leads to the formation of more stable and durable intermetallic phases, such as Cr_2Ti. Additionally, it is worth noting that the presence of a liquid phase of aluminum during processing creates favorable conditions for the diffusion of titanium through the liquid layer, which accelerates the coating formation process and improves its physical and mechanical properties.

Conclusions.

1. In this research, multifunctional SHS charges were developed to produce titanium-doped chrome coatings to strengthen the working surfaces of press tooling dies used in aggressive conditions during vulcanization of products made of elastomeric materials.
2. Using a three-factor, three-level composite asymmetric plan of the second order, optimal blends for obtaining protective coatings alloyed with titanium were developed.

3. For titanium-alloyed chrome coatings obtained on samples of steel 45, the following phases were found: $(Cr,Fe)_{23}C_6$, $(Cr,Fe)_7C_3$, Fe_2Ti, Cr_2Ti and α-solid solution of titanium and chromium in α-iron. For 40X steel, the phases are formed $(Cr,Fe)_{23}C_6$ and α-solid solution of chromium in iron with Cr_2Ti inclusions doped with titanium.

4. Multifunctional blends for heat-resistant chrome coatings have been developed: when alloyed with titanium 25% XC + 15% Cr + 20% Ti+ 34% Al_2O_3 + 2% J_2+ 4% NH_4Cl, when alloyed with silicon 24% XC + 15% Cr + 7% Si+ 49% Al_2O_3 + 2% J_2+ 3% NH_4Cl.

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БАГАТОФУНКЦІОНАЛЬНІ ШИХТИ ДЛЯ ОТРИМАННЯ ЗАХИСНИХ ПОКРИТТІВ НА ПРЕСОВОМУ ОСНАЩЕННІ В УМОВАХ СВС

В роботі розроблено багатофункціональні СВС-шихти для отримання хромованих покриттів, легованих титаном і кремнієм, з метою зміцнення робочих поверхонь матриць пресового оснащення, що експлуатуються в агресивних умовах. Пресування проводять на пресі гідравлічному вулканізаційному 100-400 2Е. з розмірами плит 400х400 нових еластомерних матеріалів на основі 10 мас.% карбонізованого волокна з ПАН (RC Helper), що значно підвищує теплоємність каучуку на основі сополімеру вінілделфториду та гексопропілену на 15 – 30% у діапазоні робочих температур від 323 до 348 К. Однією з нових та найбільш ефективних технологій виготовлення широкого спектру матеріалів, втому числі композиційних, є технологія СВС, суть якої полягає у проходженні прямого синтезу цінних в практичному відношенні сполук в екзотермічних реакціях між певними хімічними елементами. Отримання захисних покриттів на зразки в умовах СВС здійснювали на розробленій дослідно-промисловій установці ДДТУ12, яка складається з таких основних функціональних систем: реакційне обладнання; система контролю та регулювання технологічними параметрами; система утилізації газів. В роботі для нанесення покриттів використовувалися зразки зі сталей 45, 40Х. У якості реакційних агентів використовувалися суміші порошків дисперсністю 100-250 мкм. З використанням трьох факторного, трьох рівневого композиційного несиметричного плану другого порядку, розроблені оптимальні шихти за для отримання захисних покриттів легованих. Отримані покриття характеризуються багатофазною структурою та рівномірністю товщини. Для хромованих покриттів, легованих титаном отриманих на зразках зі сталі 45, виявлені фази $(Cr,Fe)_{23}C_6$, $(Cr,Fe)_7C_3$, Fe_2Ti, Cr_2Ti та α-твердий розчин титану і хрому в α-залізі. Для сталі 40Х утворюються фази $(Cr,Fe)_{23}C_6$ та α-твердий розчин хрому в залізі з включеннями Cr_2Ti, легованими титаном.

Ключові слова**:** шихта, хром, титан, покриття, пресова оснащення, саморозповсюджувальний високотемпературний синтез, вироби.